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54 Description: Procedure for the continual manufacture of
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C L A I M S O F T H E P A T E N T

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- 1) A procedure for the continual manufacture of thermoplastic polyurethanes out of polyhydroxy compounds, diisocyanates and low molecular chain extenders, in which the starting components are fed through a mixing zone and then through a reaction zone, characterized by that the starting components are mixed in a mixing zone in which a sufficient, practically total, thorough mixing takes place for the subsequent polyaddition reaction, where the product temperature is so low that for the most part a reaction of the components is avoided and the mixture is subsequently fed using a precision pump into a static mixer of such a length a diameter that the polyaddition takes place when the reaction components remain for long enough in the static mixer at a flow speed that prevents the polymers from sticking.
- 2) A procedure in accordance with claim 1 characterized by that the starting components are mixed in a static mixer.
- 3) A procedure in accordance with one of claims 1 or 2, characterized by that the starting components are fed into a static premixer, the ratio of length to diameter of which lies in the 30:1 to 500:1 range.

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- 4) A procedure in accordance with one of the claims 1 through 3 characterized by that the mixture is introduced into a second static mixer, the ratio of which between the length and diameter lies in the 100:1 to 1000:1 range.
- 5) A procedure in accordance with one or several of the claims 1 through 4 characterized by that the rate of flow is at least 3 cm/second.
- 6) A procedure in accordance with one or several of the claims 1 through 5 characterized by that the rate of flow in the second static mixer is at least approximately 1 cm/second.
- 7) A procedure in accordance with one or several of the claims 1 through 6 characterized by that the residence time in the static premixer is shorter than 10 seconds.
- 8) A procedure in accordance with one or several of the claims 1 through 7 characterized by that the residence time in the second static mixer is at least approximately ¼ minute.

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Applicant: Plate Bonn GmbH, Siemens Street, 5300 Bonn

A procedure for the continual manufacture of
thermoplastic polyurethanes

This invention concerns a procedure for the continual manufacture of thermoplastic urethanes.

How to manufacture thermoplastic polyurethanes in a continual procedure is already known. In accordance with DT-OS 1 964 834 a mixture of the starting components is manufactured in a premixer and this mixture is then dosed into a multiple screw extruder. In this procedure a lubricating agent has to be added to the starting components to provide for trouble free passage through the extruder. In some cases, however, the addition of a lubricating agent is undesirable because it has a detrimental effect on the further processing possibilities or to be more precise on the intended application of the polyurethanes. A procedure for the continual manufacture of thermoplastic polyurethane elastomers is described in DT-OS 2 447 368, in which the components are dosed directly into the feed zone of the multiple screw extruder, where a certain temperature profile has to be maintained in the extruder. Even with an optimal set up of the multiple screw extruder there is a danger of back mixing, which has the potential of disrupting the progress of the reaction,

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so that the polyurethane formed does not display totally uniform characteristics. Furthermore, in this procedure comparatively high temperatures have to be used, which are undesirable. With the use of lower temperatures it is possible to control the polyaddition process more precisely and as a result the characteristics of the polyurethane desired.

This invention is based on the nature of the task of finding a procedure for the continual manufacture of thermoplastic polyurethanes, a procedure which can be implemented in simple technical ways, which does not require high temperatures and which leads to products with exceptionally uniform characteristics.

The object of this invention is a procedure for the continual manufacture of thermoplastic polyurethanes out of polyhydroxy compounds, diisocyanates and low molecular chain extenders, in which the starting components are fed through a mixing zone and then through a reaction zone, characterized by that the starting components are mixed in a mixing zone in which a sufficient, practically total, thorough mixing takes place for the subsequent polyaddition reaction, where the product temperature is so low that for the most part a reaction of the components is avoided and the mixture is subsequently fed using a precision pump into a static mixer of such a length a diameter that the polyaddition takes place when the reaction components remain for long enough in the static mixer at a flow speed that hinders the adherence of polymers.

All appropriate contrivances may be used to mix the starting components in the mixing zone, which facilitate the most complete mixing of the components possible. Examples of this are containers with intensive stirring into which the starting components are precisely dosed. It is especially preferred for the mixing to be carried out in a static premixer. This has the advantage that it does not contain any movable parts and that an extremely good intermixing is achieved in the shortest amount of time. It is preferable for the starter products to be mixed in a static premixer, which forms the mixing zone.

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The contrivances on the market are understood by static mixers, in the sense of this invention, which amongst others are described in US-PS 3 286 992, 3 664 638, 3 704 006, 3 775 063, 3 800 985 and 3 806 097. These static mixers are pipes, the lengths of which are very long in relationship to their diameters. For example, as a lower limit for the relationship between length and diameter a ratio of 40:1 is given. One of these such relatively small ratios may be sufficient for the static premixer. Generally speaking, larger ratios are appropriate for the static mixer in which the polyaddition takes place, for example from around 100:1 to 1000:1. Mixing elements are securely fastened inside of the pipe, which bring about an exceptionally fast and complete mixing up of the components flowing through the pipe. The compounds used for the manufacture of thermoplastic polyurethanes in accordance with the state of technology are used as starting substances to carry out the procedure in accordance with the invention. In accordance with that polyhydroxy compounds, diisocyanates and chain extenders are brought in together with chain growth regulators if necessary for the reaction. The hydroxyl groups displaying polyester and polyether are suitable as polyhydroxy compounds. Polyester amides and polyester carbonates are of less significance. Especially preferred are the linear polyesters with molecular weights in the range of around 800 to 4000. The preference is to use linear polyesters, which are obtained from dicarbonic acids and diols. Examples for suitable dicarbonic acids are succinic acid, azelaic acid, sebacic acid, terephthalic acid and especially preferred is adipic acid. Examples for diols are butane-1,4 diol, butane-1,3 diol, 2-ethoxy-ethyl alcohol, hexane-1,6-diol and neopentane glycol. The polyesters can be manufactured from several of these starting substances. Polyesters obtained from E-oxycarbonic acids

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may also be used, preferably caprolacton and preferably without the addition of other polyester forming reaction components. In particular, small admixtures of other starting components, meaning dicarbonic acids and polyols are also an option though.

The compounds generally in this technical area are also used as diisocyanates, such as diphenyl methane diisocyanate, commercially available mixtures of the isomers of toluylene diisocyanates, hexamethylene-1,6 diisocyanate. Especially preferred are the toluol diisocyanates or more precisely, diphenyl methane diisocyanates known under the abbreviations TDI and MDI.

The products used in accordance with the state of technology for the manufacture of polyurethanes are also used as chain extenders, in particular low molecular diols with 2 to 10 C-atoms in the chain such as butane-1,4 diol, butane-1,3 diol, propane-1,2 diol, ethylene glycol, hexane-1,6 diol, neophenthylglycol. Diols that contain the ether acid oxygen atoms in the chain such as diethylene glycol, triethylene glycol, etc., may also be used.

The products customarily used in this technical area are also used as chain growth regulators, such as mono basic aliphatic alcohols or amino alcohols with approximately 10 to 14 carbon atoms. Especially preferred is dodecane as in accordance with the state of technology.

The polyhydroxy compounds and diisocyanates are used in roughly stoichiometric quantities. A low excess of one or the other components is possible. The amount of the chain extender and the chain growth regulator is directed towards the desired characteristics of the polyurethane to be manufactured.

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The starting components may be added to the catalysts, stabilizers, extenders etc. customarily used in this area.

To implement the procedure in accordance with the invention the starting substances are charged into a mixing zone, preferably into a static premixer. In addition, the chain extender and if necessary, the chain growth regulator of the polyhydroxy compound can first be mixed in in the desired measured ratios, because no undesired reaction occurs between these groups of compounds. The diisocyanate components, however, have to added separately to the premixer. The task of the static mixer is to achieve the most extensive mixing of the components possible in the shortest possible amount of time, and to a great extent, however, to avoid a reaction between the components. For this reason a high flow speed and a short residence time are desired. It is appropriate for the residence time to total less than 10 seconds, preferably less than 5 seconds, and especially preferably less than 2.5 seconds.

It is appropriate for the flow speed to total at least 3 cm/second, preferably at least 5 cm/second and especially preferably approximately 10cm/second. The upper limit for the flow speed is not as critical and the guarantee of an easy implementation of the procedure essentially depends on it. For example, the upper limit for the flow speed in the static premixer may lie at around 100 cm/second, preferably at the highest at around 80 cm/second and especially preferably preferred at the most at 50 cm/second.

As already outlined above, the ratio of length to diameter of the static mixer is large. It is functional for the ratio to be at around 30:1, preferably at least at around 40:1, and especially preferably at least at around 50:1. The upper

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limit is not particularly critical. It is fundamental that there is a total intermixture of the components. There is practically no danger of the polymers adhering to the wall in the premixer, because the temperature is kept so low that a reaction does not occur there to any mentionable degree. Generally speaking it is however appropriate for the ratio in the static premixer not be above 500:1, preferably not above around 300:1 and especially preferably not above around 100:1. The absolute quantities are dependent on the capacity of the plant. At a flow through rate of, for example, 30 kg per hour, a premixer having a length of approximately 400 mm and an internal diameter of around 8 mm is suitable for example.

The temperature of the reaction components in the premixer is kept so low that so far as possible, a reaction is prevented. Certain increased temperatures are required because the starter products to some extent stay in a solid state at normal temperatures. In this case they are melted and mixed with each other in a liquid aggregate state. On an individual basis then the temperatures are directed towards the melting points and the mixed melting points of the respective starting substances used. Since hardly any polyaddition reaction occurs in the premixer, there is practically no increase at all in the viscosity and the flow is easily possible. It is therefore not required that the starting components be fed into the premixer under high pressure, which makes implementation of the procedure technically much simpler. The dosing of the individual components is done in the known ways using precision dosing points, which are controlled using the known control systems.

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The mixture leaving the static premixer is fed using a precision pump into a second static mixer where the polyaddition reaction takes place. Certain gear pumps are particularly suitable as precision pumps. Other pumps may also be used, such as precision reciprocating pumps. It is fundamental that the precision pumps always work at full capacity, meaning that there is essentially no back-flow.

An undesirable and uncontrollable reaction is avoided in this area of the implementation of the procedure because of the relatively high flow through speed through the premixer and the immediate transportation of the mixture away by the precision pump. Naturally, work is done throughout the whole area with the exclusion of moisture and functionally in a protective atmosphere (nitrogen), as this is also the case in the known set-ups for the continual manufacture of polyurethanes. The mixture leaving the precision pump reaches a second static mixer in which the polyaddition takes place at an increased temperature. The polyaddition reaction is exothermic. It is functional to feed in heat at the entry of the second static mixer to get the reaction started. Outside of this it may then be necessary dissipate the heat to keep the temperature within the desired range. In order to achieve total polyaddition the second static mixer has to be considerably longer than the static premixer. The second static mixer is also distinguishable through a high ratio of length to diameter. It is functional for the ratio to be at least around 100:1, preferably at least around 200:1 and especially preferably at least 400:1.

The upper limiting value for this ratio is, once again, not critical. It is dependent on the other parameters, of these parameters in particular when the reaction is finished to the desired extent. Naturally, it makes no sense to select the length so that the polyurethane still has to

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be squeezed through the pipe following practically total polycondensation. Generally speaking the upper limit for the ratio of length to diameter lies at around 1000:1, preferably at around 800:1 and especially preferably at around 600:1.

It may be functional for the second static mixer, in which the polyaddition takes place, not to have the same diameter along its entire length. Since the viscosity increases as the polyaddition progresses, it may be functional to expand the diameter of the second static mixer as the polyaddition progresses. This may be done gradually but pipes with different diameters may also be lined up adjacent to each other. The above given values for the ratios of length to diameter are based in these types of cases on the average ratio of length to diameter.

The absolute measurements are dependent, as in the static premixer, on the capacity of the plant. At a capacity of, for example 30 kg/hour, a static mixer with a length of 1000 cm and an average diameter of 2 cm proved itself to be suitable. Work may however, in this case, for example also be done with a static mixer with a length of around 600 cm and an average diameter of around 1 cm.

The measurements are selected in such a way that a sufficient flow speed is achieved at which the adherence of reaction products to the walls of the mixers is avoided. Suitable average flow speeds lie at at least around 1 cm/second, preferably at at least around 2 cm/second and especially preferably at at least 4 cm/second. The upper limit for the flow speed is not particularly critical. It is for the most part determined by the viscosity of the polyurethane obtained because this relatively highly viscous product is for natural reasons not able to flow so fast through the mixer the way that a low-viscosity liquid can. Generally speaking, the upper limit for the flow speed

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in the second static mixer is not above 40 cm/second, preferably not above 20 cm/second and especially preferably not above 10 cm/second.

The residence times in the second static mixer, in which the polyaddition takes place, are set in such a way that the polyaddition is done dependent on the temperature of the reaction mixture used. It is functional for the residence time to total at least around half a minute, preferably at least around half a minute and especially preferably at least around one minute. The upper limit of the residence time is for the most part determined from an economic standpoint. So a temperature is chosen at which a not overly long residence time is required so that mixers are not in use for too long. Examples for the upper limit of the residence time are approximately 10 minutes, preferably around 5 minutes at the highest and especially preferably around 2 minutes at the highest.

The temperatures of the reaction mixtures are, as already outlined, selected so that a rapid polycondensation takes place. In principle, and generally speaking the higher the reaction temperature the shorter the residence time.

The quantities dosed into the second static mixer by the precision pump have to coordinate with the quantities of the starting product dosed into the premixer. This is achieved through the known appropriate regulating and controlling devices.

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After leaving the mixers, in which the polyaddition is done, the polyurethane is expediently exposed to post-tempering. The extent of the post-tempering fits in known ways with the extent of the polyaddition carried out in the reactor. The closer the polyaddition in the reactor comes to being final, the lower the requirement for post-tempering. Conversely, it is the nature of things that post-tempering must be carried out for longer if the polyaddition is not pushed far enough along in the reactor. These relationships are known to the specialists in the polyurethane manufacturing industry. Granuals may be made and then there is further processing in the customary ways into the different end products such as foils, hot melt glues, solubilizing adhesives, etc..

The devise for implementation of the procedure in accordance with the invention is explained using schematics in the enclosed drawing. The reservoir 1 contains the diisocyanate. The reservoir 2 contains the mixture of the polyhydroxy compounds and other components of the reaction mixture with the exception of the diisocyanates. These components are charged in through dosing pumps 3 and 4, pneumatic regulating valves 5 and 6. Regulator 7, more precisely 7a, control the valves in connection with the meters, which are not shown, which establish the actual amounts of the starting components fed in. In this way mixing of the components is done, in which however, the reaction is, for the most part avoided. The mixture leaving the static premixer 8 is fed using the precision pump 9 into the second static mixer 10, which may be heated or cooled, and in which the polyaddition takes place. The pump 9 is run by a controllable motor 11, which is controlled by an automatic control device 12. The control is done dependent on the quantities allowed by the static premixer 8 and the desired flow speeds. The heating and/or cooling contrivances of the static mixer are controlled by automatic control devices in the desired way. The polyurethane leaving the static mixer 10 is fed to known contrivances for further processing.

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Example 1

A mixture of 100 parts by weight of a polyester, manufactured from adipic acid and butane-1,4 diol with the OH number 56, 3.375 parts by weight butane-1,4 diol, 3.375 parts by weight butane-1,3 diol and 0.93 parts by weight n-dodecanol is dosed with 38.75 parts by weight, diphenyl-4,4 methane diisocyanate into the static premixer using dosing pumps. The temperature is at around 50 °C. Using the feed pump the mixture is conveyed into a second static mixer (reactor). The temperature profile in the reactor is approximately as follows:

1 st	zone	approximately	120 °C
2 nd	zone	approximately	100 °C
3 rd	zone	approximately	100 °C

The three zones have approximately the same lengths. The total residence time lies at between 6 and 8 minutes. The polyurethane leaving the second static mixer is exposed to a post-tempering in the heater at 110 °C over 6 to 1 hours.

Example 2

A mixture of 100 parts by weight of a polyester, manufactured from adipic acid and ethane diol/butane diol in a ratio of 7/3 with 12.5 parts by weight neopentylglycol is dosed with 42.5 parts by weight diphenylmethane-4,4 diisocyanate into the premixer. The temperature should not exceed 60 °C.

Using the feed pump the mixture leaving the premixer is conveyed into the second static mixer (reactor). The temperature profile in the reactor is approximately as follows, where the three zones have approximately the same lengths:

1 st	zone	approximately	135 °C
2 nd	zone	approximately	110 °C
3 rd	zone	approximately	120 °C

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The total residence time is 8 to 10 minutes. The polyurethane leaving the second static mixer is post-tempered for 6 to 12 hours at approximately 110°C.

Example 3:

A mixture of 100 parts by weight of the polyester described in example 1, 3.375 parts by weight butane-1,4 diol, 3.375 parts by weight butane-1,3 diol and 0.66 parts by weight n-dodecane as well as 32.0 parts by weight diphenylmethane-4,4 diisocyanate are dosed into the static premixer using dosing pumps. The temperature in the static premixer is at around 50 °C.

Using a precision toothed wheel spin pump the mixture is conveyed into the second static mixer. The temperature profile in the second mixer (reactor) is at approximately 107 to 120 °C throughout the entire area. The ratio between length and diameter of the reactor is 580:1. The throughput is around 30 kg/hour. The residence time is approximately 1 minute. The polyurethane leaving the second static mixer is exposed to post-tempering in a heater at 110 °C for 4 to 6 hours.

Example 4:

A mixture of 6009 parts by weight of a polyester manufactured from adipic acid and hexane-1,6 diol, 528 parts by weight butane-1,3 diol and 54.6 parts by weight n-dodecane as well as 2308 parts by weight diphenylmethane-4,4 diisocyanate are dosed into the static premixer using a dosing pump. The temperature is at around 50 °C. Using the pump described in example 3 the mixture is conveyed into the second static mixer. The temperature profile in the second static mixer (reactor) totals around 110 to 120 °C across the whole reactor. The total residence time in the reactor totals around 25 kg per hour. The dimensions of the reactors and of post-tempering are as given in example 3.

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